

Proc. Eurosensors XXVI, September 9-12, 2012, Kraków, Poland

## Screen-Printed Potentiometric Sensors for Chloride Measurement in Soils

A. Cranny<sup>a\*</sup>, N.R. Harris<sup>a</sup>, N.M. White<sup>a</sup>, E. Barrett-Lennard<sup>b</sup>,  
N. Coles<sup>b</sup>, M. Rivers<sup>b</sup>, K. Smettem<sup>b</sup>, J. Wu<sup>c</sup>

<sup>a</sup>*School of Electronics and Computer Science, University of Southampton, Highfield, Southampton, SO17 1BJ, UK*

<sup>b</sup>*Centre of Excellence for Ecohydrology, University of Western Australia, Crawley, Perth, WA 6009, Australia*

<sup>c</sup>*College of Environment and Resources Sciences, Zhejiang University, Hangzhou, Zhejiang Province, 310058, P. R. China*

---

### Abstract

Screen-printed potentiometric sensors have been developed to detect the presence of chloride ions within moist soils. In work previously published by some of the authors, sensor lifetimes in excess of 1 year have been established with near Nernstian response to chloride ions ( $-49.8 \pm 1.7$  mV per decade) over the range 0.1 mM (3.55 mg/L) to 200 mM (7.09 g/L). The sensors demonstrate the ability to measure transient changes in soil chloride concentration allowing chloride retention times in different types of soil to be determined.

© 2012 The Authors. Published by Elsevier Ltd. Selection and/or peer-review under responsibility of the Symposium Cracoviense Sp. z.o.o. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Chloride sensor; hydrology; potentiometric sensor; screen-printed sensor; soil measurement, bad template.

---

### 1. Introduction

Of global concern is the increasing storage of agricultural chemicals in soils and various surface and subsurface water bodies arising from the over-application of fertilisers. Chemical species such as nitrates and chlorides impact on crop growth and adversely on the quality of water supply for both communities and various commercial activities. From the hydrological perspective, there is a plethora of literature concerning the possible origins and sources of runoff. A common technique to determine the residence and transits times of runoff is to use conservative tracers sampled at points (mostly limited spatially and temporally) supported by simple input-output models [1, 2]. There are existing spatial models for small

---

\* Corresponding author. Tel.: +44-238-059-9204; fax: +44-238-059-2901.

E-mail address: [awc@ecs.soton.ac.uk](mailto:awc@ecs.soton.ac.uk).

scales (<1 km<sup>2</sup>) which attempt to predict runoff sources and therefore chemical transport [3, 4], but field campaigns have been limited (due to costs in equipment/labour) and sampling is restricted to physical sampling at each nodal point [5, 6].

Currently catchment scale models designed to predict the impacts of land use and land covers on hydrology and water quality are limited by a lack of ‘ground-truth’ data across both spatial and temporal scales [7]. Limiting factors include the costs of existing field instrumentation and labour to maintain such networks, both of which result in sparse sampling. Hence the ‘Holy Grail’ of hydrological and water quality research is to secure quality data across all scales to determine the spatial and temporal sources of storm runoff and simultaneously for various chemical species (*e.g.* Cl<sup>-</sup>, NO<sub>3</sub>), allowing:

- Identification of ‘hot spots’ of both surface and subsurface sources which contribute towards runoff and chemical transport which are key to devising better land – water management strategies;
- Improved models of tracking water and chemical transfer across scales.

Screen-printed chemical sensors can potentially address these issues and when coupled with wireless technology and localised energy harvesting, could provide a cheap deployment solution for large-scale hydrological monitoring.

## 2. Principle of operation

The chloride sensor is in essence the functional part of the standard Ag/AgCl electrochemical reference electrode and generates a potential based on changes in the concentrations of the constituent components of the dissociation reaction:



The steady state or equilibrium potential (E) associated with this reaction is related to the concentrations (more accurately, the activities) of the reactant and dissociation products and can be expressed by the Nernst equation [8]:

$$E = E^{\theta'} + \left( \frac{RT}{nF} \right) \ln \left( \frac{C_{\text{AgCl}}}{C_{\text{Ag}} C_{\text{Cl}^{-}}} \right) \quad (2)$$

Where E<sup>θ'</sup> is the electrode formal potential (V), R is the molar gas constant (8.31 J K<sup>-1</sup> mol<sup>-1</sup>), T is the absolute temperature (K), n is the stoichiometric number of electrons transferred in the reaction (n = 1), F is the Faraday constant (96485 C mol<sup>-1</sup>) and C<sub>x</sub> is the concentration of species x. Because silver chloride is a sparingly soluble salt its concentration should ideally remain constant in aqueous media. Likewise, the concentration of silver should also remain constant since it is in a solid phase. Hence, by substituting values for the various parameters at a temperature of 25°C, the equation above may be rewritten as:

$$E = E_0 - 0.0592 \log C_{\text{Cl}^{-}} \quad (3)$$

Here, E<sub>0</sub> is an offset potential (V) based on the electrode formal potential but also accounts for the different, though constant, concentrations of silver and silver chloride. Thus, under ideal conditions and at an operating temperature of 25°C, the measured electrode potential (E) theoretically decreases by approximately 59 mV for every decade change in chloride ion concentration.

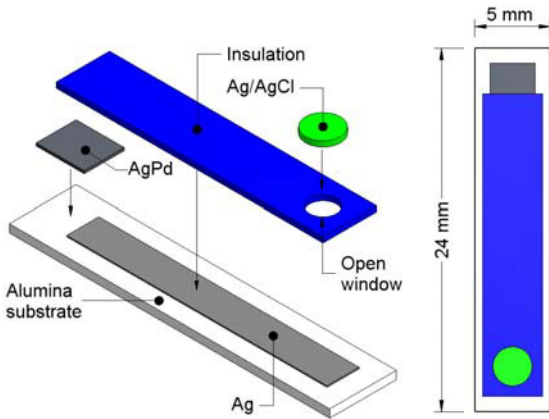


Fig. 1. Schematic of a single potentiometric chloride sensor composed of a number of screen-printed layers.

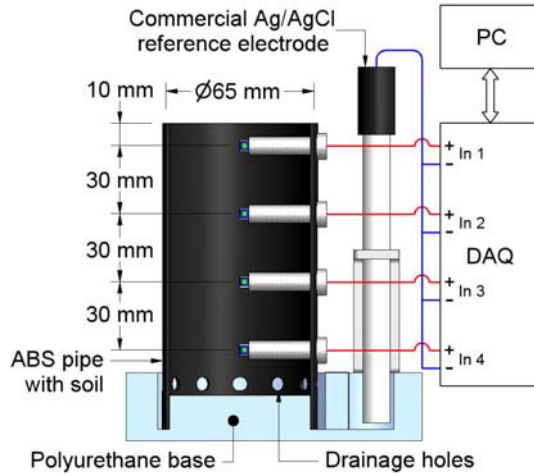


Fig. 2. Schematic showing cross-sectional view through soil column apparatus and sensor positions.

### 3. Experimental

Potentiometric chloride sensors have been developed under clean-room conditions that are composed of a layer of proprietary AgCl material screen-printed upon a silver electrode as shown in Fig. 1 [9]. To demonstrate their ability to detect chloride transport through soil, an experiment was conducted using a 65 mm diameter, 120 mm high column of a sterile sandy clay loam soil containing less than 5% organic matter (B+Q, top soil loam for beds, borders and lawns, produced to British Standard BS3882 Top Soils 1994) in which 4 sensors were inserted down the column length at locations 3 cm apart, as shown in Fig. 2. Potentials generated by each sensor were measured with respect to a commercial Ag/AgCl reference electrode (VWR GelPlas, 3.5M KCl) located in the drainage channel at the base of the column, using a multi-channel data acquisition system (NI DAQPad 6015) controlled through bespoke software (LabView). Sensor potentials were measured continuously at a rate of 1 kHz, but readings were only logged to disk at a rate of one reading per sensor every 5 seconds, with each reading being the average of 100 successive samples.

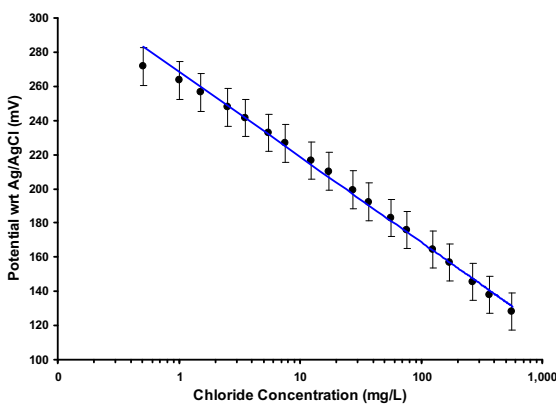


Fig. 3. Calibration data for 7 potentiometric chloride sensors showing average values and spread.

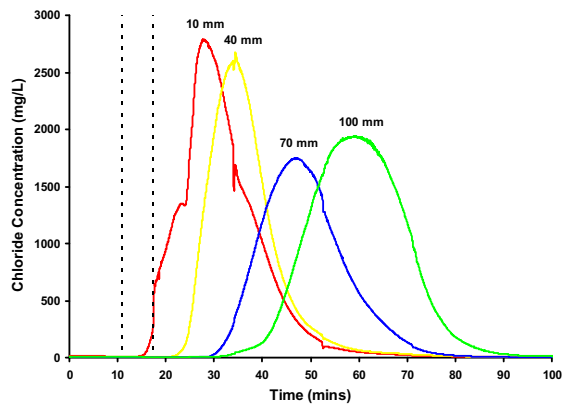


Fig. 4. Measured chloride profiles as function of depth. Broken lines indicate addition of chloride solution.

Test solutions were applied to the top of the soil column using tension infiltrometers (Mini Disk, Decagon Devices), enabling flow rates to be controlled and maintained. Chloride solutions were prepared by dissolving anhydrous calcium chloride (> 93%, Sigma Aldrich) in deionised water (Elga Purelab Option, reverse osmosis water purification system, >15 M $\Omega$ -cm). Prior to performing the soil column experiment, the sensors were calibrated by measuring their potentials in various chloride solutions of known concentration ranging over 3 orders of magnitude from 14  $\mu$ M (0.5 mg/L) to 15.7 mM (555 mg/L) as shown in Fig. 3. This revealed that the sensors had a sub-Nernstian response to chloride ions with an average sensitivity of  $-48.6 \pm 1.0$  mV per decade change in chloride concentration (sensor sample size of 7), though individual sensor calibration coefficients were used to convert measured potentials to equivalent chloride ion concentrations.

#### 4. Results

Fig. 4 shows a typical set of results when a 100 mM chloride solution (3,545 mg/L) was added to the top of the soil column with a flow rate of 5.4 mL/min. Prior to and after the chloride 'pulse', deionised water was run through the soil column at an average flow rate of 5.6 mL/min. The data clearly shows the broadening of the chloride 'pulse' as it travels through the soil and that in general the maximum chloride concentration measured reduces with depth. The seemingly anomalous higher concentration detected by the sensor located at a depth of 100 mm when compared to that detected by the sensor located at a depth of 70 mm can be explained by difference in the paths taken by solutions when moving through a heterogeneous medium. Nevertheless, the sensors and experimental technique demonstrate the potential to measure and interpret key hydrological parameters such as transit time and soil retention effects.

#### References

- [1] Kirchner JW, Tetzlaff D, Soulsby C. Comparing chloride and water isotopes as hydrological tracers in two Scottish catchments. *Hydrological Processes* 2010;**24**:1631–1645.
- [2] Dunn SM, Birkel C, Tetzlaff D, Soulsby C. Transit time distributions of a conceptual model: their characteristics and sensitivities. *Hydrological Processes* 2010;**24**:1719–1729.
- [3] Beven KJ. TOPMODEL: A Critique. *Hydrological Processes* 1997;**11**:1069–1085.
- [4] Grayson RB, Western AW, Chiew FHS, Blöschl G. Preferred states in spatial soil moisture patterns: Local and nonlocal controls. *Water Resources Research* 1997;**33**:2897–2908.
- [5] Western AW, Grayson RB, Green TR. The Tarawarra project: High resolution spatial measurement, modelling and analysis of soil moisture and hydrological response. *Hydrological Processes* 1999;**13**:633–652.
- [6] Summerell GK, Tuteja NK, Grayson RB, Hairsine PB, Leaney F. Contrasting mechanisms of salt delivery to the stream from three different landforms in South Eastern Australia. *J Hydrology* 2006;**330**:681–697.
- [7] Grayson RB, Moore ID, McMahon TA. Physically based hydrologic modeling: 2. Is the concept realistic? *Water Resources Research* 1992;**28**:2659–2666.
- [8] Brett CMA, Brett AMO. *Electrochemistry principles, methods and applications*. Oxford: Oxford University Press, 2005.
- [9] Cranny A, Harris NR, Nie M, Wharton JA, Wood RJK, Stokes KR. Screen-printed potentiometric Ag/AgCl chloride sensors: Lifetime performance and their use in soil salt measurements. *Sensors and Actuators A* 2011;**169**:288–294.